Transistors and Light Emitters from Single Nanoclusters

Horst Weller*

What must the perfect transistor be able to do? From a chemist's or physicist's point of view this question can easily be answered: It must be able to operate with a single electron. Recently the groups of Alivisatos and McEuen from Berkeley succeeded in putting into practice such a single-electron transistor (SET) with CdSe semiconductor nanocrystallites of approximately 5 nm in size synthesized by wet chemical methods.[1] Owing to their size-dependent material properties, the class of substances of these nanoparticles enjoys great popularity in different branches of chemical and physical research.[2–9] The schematic construction of this SET is shown in Figure 1. It consists of a highly doped, electrically conducting Si substrate, the surface of which is covered with a thin, electrically insulating layer of SiO_2. By a sophisticated lithographic and evaporating technique two gold wires were applied in a way that their ends were separated by only about 10 nm. With alkane dithiols serving as a kind of molecular adhesive, the CdSe nanoparticles out of the solution were fixed to these wires. Thus, the gold wires are totally covered with nanoparticles, some of which are placed right between the gold wires.

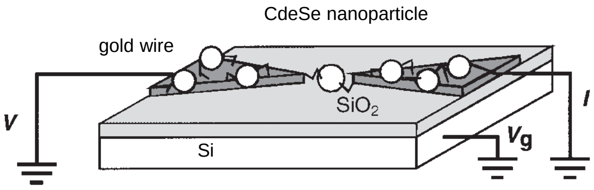

Figure 1. Schematic construction of a single-electron transistor. A CdSe nanoparticle is placed between two gold wires.

The "trick" is now the following: The tunnel current which can flow from one gold tip over the particles into the other gold tip depends drastically on the tunnel distance. As a result, the electrons choose only one single way through the particle, that with the shortest tunnel barrier, whereas other possible paths of current are practically of no importance. This effect has become known for quite some time from scanning tunnel microscopy.

By means of the construction of Alivisatos and McEuen the current I between the gold contacts can be measured as a function of the applied voltage V and a gate voltage V_g applied over the Si substrate. The authors could show that the charge transport through the nanocrystallite is determined by two effects which are due to the small dimensions of the particles. Let us consider two macroscopic semiconductors or metals in electric contact after adjusting the equilibrium: Both solids have the same electrochemical potential (Fermi level). A single electron can easily be transmitted from one solid to the other one without any perceptible change in the energetics of the system. Such exchange processes in which the natural fluctuation or the dynamic equilibrium between both solids is expressed occur permanently. Let us imagine that the contact takes place between a macroscopic solid (gold wire) and a nanoparticle. By taking off one single electron from the wire, its energy will not be changed. Owing to the very small surface capacity of the nanoparticle (C) there will be a noticeable charge ΔU according to the capacitor law, which will result in an energy increase of ΔE_C [Eqs. (1), (2)].

$$\Delta U = e/C \tag{1}$$

$$\Delta E_C = e^2/2C \tag{2}$$

The Fermi level of the wire must be augmented by applying a voltage of at least ΔU in order to transfer one electron on the particle. This effect is called the Coulomb blockade. Values typical of a particle with a diameter of a few nanometer are to be found in an area of several 10 meV. This phenomenon is amplified especially in semiconductors by the occurrence of the size-quantization effect (SQE). The nanoparticles represent a state of matter in the transition region between solids and molecules, in which the quasi-continuum of the energy bands has dissolved and an energy diagram with discrete molecular-orbital-like levels already exists.

From a molecular point of view it becomes clear that particular minimum voltages have to be applied to the electric contact in order to fill up gradually levels which are separated by a definite energy difference (ΔE_{SQE}; comparable with the first and the second oxidation or reduction potentials of a molecule). The difference in the elctrochemical potential of a nanoparticle with $N+1$ electrons (μ_{N+1}) and one with N electrons (μ_N) is given by Equation (3).

$$\Delta\mu = \mu_{N+1} - \mu_N = \Delta E_C + \Delta E_{SQE} \tag{3}$$

This transport barrier $\Delta\mu$ can be overcome by applying the grid voltage or a bias voltage, as can be seen from Figure 2. In a situation as that shown in Figure 2a there would be no current flow, as the attainable levels of the nanoparticle are populated by electrons. Only after increasing the potential at one end of the wire—that is, by applying an external voltage—can the electron transport take place as shown in Figure 2b. If the voltage is increased up to the level of the next, non-occupied orbital, the current raises abruptly. From this results a staircaselike current–voltage characteristic.

It is also possible to induce current flow by applying a gate voltage, thus lowering the LUMO (*l*owest *u*noccupied *m*olecular *o*rbital) in the particle to a degree that the electrons can jump over (Figure 2c). If the gate voltage is further increased in this direction, the former LUMO is now

---

[*] Prof. Dr. H. Weller
Institut für Physikalische Chemie der Universität
Bundesstrasse 45, D-20146 Hamburg (Germany)
Fax: (+49) 40-4123-3452
E-mail: weller@chemie.uni-hamburg.de

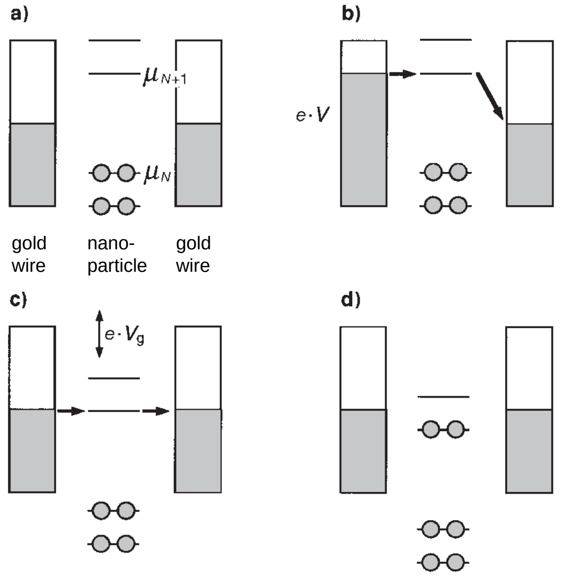

Figure 2. Energy diagram in a single-electron transistor under different conditions of external polarization (see text).

populated by electrons and the current flow breaks down until the next free orbital is brought to the Fermi level of the contact (Figure 2d). The current–voltage curve shows periodical increases and decreases (Coulomb oscillations). Such experiments allow a unique spectroscopy of the electronic states in such nanocrystallites, and they can be considered as an important advance towards molecular electronics.

Same attention should be given to fluorescence spectroscopic investigations on single semiconductor nanoparticles which have also been reported in the recent past.[10–15] CdS or CdSe particles in extremely thin coating were applied on a quartz sheet which could be moved in the x,y plane through a strongly focused laser spot. When the laser beam hits a particle, fluorescence is observed, otherwise there is darkness. Thus, a topography of the sample can be made for which the lateral resolution is not determined by the size of the particles, but by the diameter of the focused laser beam. Then it was possible to approach a position where a particle was detected and to record the focused fluorescence light in spectral decomposition. A fluorescence spectrum of a single CdS particle of approximately 6 nm in size obtained in this way at 15 K is shown in Figure 3.[14] One can see a very sharp main line and two smaller bands on the long-wavelength side; the distance of the latter exactly conforms to the progression of the LO phonon in CdS. On the shot-wavelength side of the main peak there is a further small band which is assigned to the light emission of a biexciton-like state (consisting of two electrons and two holes in one particle).

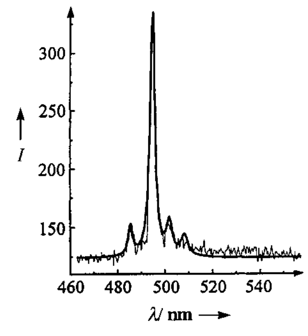

Figure 3. Fluorescence spectrum of a single, 6 nm large CdS particle at 15 K. Intensity I is given in arbitrary units.

In such single-particle fluorescence measurements, processes could be detected for the first time which have been asserted for quite some time to be the explanation for the very complex charge-carrier recombination in such nanoparticles. In accordance with this, there exist "dark states" into which an excited particle can relax and from which no light emission can result. This could be, for instance, an ionized particle or a particle in which the charge carriers are captured in some sort of surface traps. After a certain time the particle can recover from this state, and the radiating recombination with emission of fluorescence quanta starts again. In classical kinetic investigations on an ensemble of particles, this would be observed in a reduced quantum yield and called a competing reaction path. When studying a single particle one can see this competing process in time fluctuations of the fluorescence. For a certain amount of time, the particle is able to fluoresce, then it "switches off" and remains dark for some time then starting again to fluoresce. Thus, one observes the level statistics directly in the time domain. Furthermore, excitation and trapping of electrons can result in the formation of local electric fields which influence the energy of the fluorescence photons. Combined with the mentioned time fluctuations, jumping of the fluorescence bands on the wavelength scale and/or line broadening may be possible. In this connection one may devise interesting modulation experiments on a nanoscopic scale.

These examples show up to which dimensions solids can be diminished and investigated with today's methods as holders of functions with size-dependent properties. If one thinks of the possibility of ordering nanoparticles in complex superstructures by self-organizing processes,[16] one recognizes the complexity and the consequences of nanochemistry in modern material research.

German version: *Angew. Chem.* **1998**, *110*, 1748–1750

Keywords: clusters · colloids · nanostructures · semiconductors

---

[1] D. L. Klein, R. Roth, A. K. L. Lim, A. P. Alivisatos, P. L. McEuen, *Nature* **1997**, *389*, 699–701.

[2] A. Henglein, *J. Phys. Chem.* **1993**, *97*, 5457–5471.

[3] H. Weller, *Angew. Chem.* **1993**, *105*, 43–55; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 41–53

[4] H. Weller, *Adv. Mater.* **1993**, *5*, 88–95.

[5] H. Weller, A. Eychmüller, *Adv. Photochem.* **1995**, *20*, 165–216.

[6] A. P. Alivisatos, *J. Phys. Chem.* **1996**, *100*, 13226–13239.

[7] A. P. Alivisatos, *Science* **1996**, *271*, 933–937.

[8] L. E. Brus, *Appl. Phys. A.* **1991**, *53*, 465–474.

[9] L. E. Brus, *J. Phys. Chem.* **1994**, *98*, 3575–3581.

[10] S. A. Blanton, A. Dehestani, P. C. Lin, P. Guyot-Sionnest, *Chem. Phys. Lett.* **1994**, *229*, 317–322.

[11] S. A. Blanton, M. A. Hines, P. Guyot-Sionnest, *Appl. Phys. Lett.* **1996**, *69*, 3905–3907.

[12] M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, L. E. Brus, *Nature* **1996**, *383*, 802–804.

[13] S. A. Empedocles, D. J. Norris, M. G. Bawendi, *Phys. Rev. Lett.* **1996**, *77*, 3873–3876.

[14] J. Tittel, W. Gohde, F. Koberling, T. Basché, A. Kornowski, H. Weller, A. Eychmüller, *J. Phys. Chem. B* **1997**, *101*, 3013–3016.

[15] J. Tittel, W. Göhde, F. Koberling, A. Mews, A. Kornowski, H. Weller, A. Eychmüller, T. Basché, *Ber. Bunsenges. Phys. Chem.* **1997**, *101*, 1626–1630.

[16] H. Weller, *Angew. Chem.* **1996**, 108, 1159–1161; Angew. *Chem. Int. Ed. Engl.* **1996**, *35,* 1079–1081.